2001

Magnetic and Calorimetric Studies on the Non-Linear Optical Material Ga1-xMnxS

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Abstract

The new layered III-VI Diluted Magnetic Semiconductors (DMS) are 2-D systems containing transition metal ions (e.g. Mn, Fe, Co, etc.) in a III-VI semiconducting host (e.g. GaSe, GaS, etc.). The III-VI DMS $Ga_{1-x}Mn_xSe$ exhibits a strong red emission at 1.804 eV attributed to the Mn ions. The III-VI semiconductors are known for their remarkable nonlinear optical properties and are promising materials for photoelectronic applications. This work also complements the enormous progress in the II-VI DMS and the more recent efforts in the Mn doped III-V DMS systems.

In a manuscript published last summer, Pekerak et al present magnetization data on the III-VI DMS $Ga_{1-x}Mn_xSe$ that is strikingly different from any of the II-VI DMS. A key feature is a broad peak in the magnetization versus temperature data between 120 and 195 K that is ascribed to direct Mn-Mn pairs. This is a fundamentally different behavior that that observed in the heavily studied II-VI DMS. Except for this single publication, no previous magnetic or calorimetric measurements on III-VI DMS have been reported.

Recently, we conducted magnetic measurement on $Ga_{1-x}Mn_xS$. Its magnetic behavior was remarkably different from $Ga_{1-x}Mn_xSe$ and II-VI DMS. The prominent broad peak between 120 and 195 K in the magnetization of $Ga_{1-x}Mn_xSe$, ascribed to direct Mn-Mn pairs, is absent in the $Ga_{1-x}Mn_xS$ data. This suggests there are no direct Mn-Mn pairs in the GaS system. However, the magnetization of $Ga_{1-x}Mn_xS$ does show a sharp cusp at 11.3 K (an order of magnitude higher than the spin-glass transition in $Cd_{1-x}Mn_xS$) suggesting that a similar mechanism with Mn-Se-Mn pairs may be present in $Ga_{1-x}Mn_xS$. The exchange interactions in $Ga_{1-x}Mn_xSe$ and $Ga_{1-x}Mn_xS$ (with lower symmetry than the II-VI and III-V DMS) are more complex and exhibit significantly different magnetic properties. The magnetic and calorimetric measurements will provide key information for unraveling some of the observed novel magnetic effects.

Calibration was done on the computer-controlled ac-temperature calorimeter, which was just constructed at the University of North Florida for use down to 0.5 K using liquid He in a pumped ^3He Cryostat. This will help to deptermine how the Mn ions behave individually, as pairs in different configurations (e.g. Mn-Mn, Mn-Se-Mn, Mn-Ga-Se-Mn, etc.), as well as long-range cooperative interactions in the bulk crystals.

Measurements were conducted for a week at the National High Magnetic Field Laboratory (NHMFL) to study the magnetic properties of $Ga_{1-x}Mn_xS$ at temperatures down to 0.5 K in fields up to 30+ Tesla. Initial measurements at the NHMFL have already been conducted on $Ga_{1-x}Mn_xSe$ for comparison.

Introduction

Calibration of the Cernox 70 ohm Sensor

Before any measurements could be made, it was necessary to calibrate our thermometer. Lake Shore Cryotronics, Inc. provides calibration services for all types of cryogenic temperature sensing elements. Lake Shore has found that Cernox model sensors can be accurately fit to a polynomial equation based on the Chebychev polynomials. With a Lake Shore calibrated Cernox 30 ohm resistor and a sensitive temperature controller, we were able to obtain accurate temperature measurements to use in the calibration of the Cernox 70 ohm sensor.

Chebychev Polynomials

The Chebychev polynomial of degree n is denoted by $T_n(x)$ and is defined recursively by:

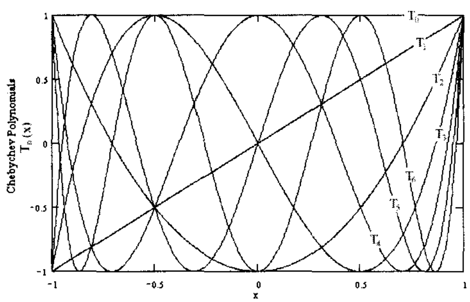
$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_{n+1}(x) = 2*x*T_n(x) - T_{n-1}(x),\ n \geq 1.$$

These polynomials are alternately defined by the formula:

$$T_n(x) = \cos(n*\arccos(x)) \qquad (1.1)$$

The first 7 Chebychev polynomials are shown in Figure 1.1.

Figure 1.1. Chebychev polynomials $T_0(x)$ through $T_6(x)$.



LabView and SigmaPlot

Lakeshore Cryotronics has found that the a linear combination of the Chebychev polynomials provides a good fit to the Cernox Resistors data, thus necessary in obtaining a calibration curve. Our problem can be described as such: given a set of observation data, find a set of coefficients a_j, such that:

$$t_i = \sum_{j=0}^{k-1} a_j * T_j(x_i) \qquad i=0,1,\ldots,n-1. \qquad (1.2)$$

where:

t is the temperature in kelvin,
A is the set of coefficients,
k is the number of coefficients, in our case k= 9, and
T_j is the j^{th} Chebychev polynomial as defined in equation (1.1).

Our observation data was resistance (X values). These values were first normalized using the equation:

$$x = \frac{(Z-L) - (U-Z)}{U-L} \qquad (1.3)$$

where:
Z = log (Resistance) = log (X),
L represents the lower limit of the variable Z and U is the upper limit of the variable Z.

This normalization produces a variable x such that -1 # x # 1. These values of x were then used to produce a matrix **H**. To build **H** we set each column to the independent functions evaluated at each x value. So if there were n resistance values (hence n x values), then **H** would be as follows:

$$\mathbf{H} = \begin{bmatrix} T_0 x_0 & T_1 x_0 & T_2 x_0 & T_3 x_0 & T_4 x_0 & T_5 x_0 & T_6 x_0 & T_7 x_0 & T_8 x_0 \\ T_0 x_1 & T_1 x_1 & T_2 x_1 & T_3 x_1 & T_4 x_1 & T_5 x_1 & T_6 x_1 & T_7 x_1 & T_8 x_1 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ T_0 x_{n-1} & T_1 x_{n-1} & T_2 x_{n-1} & T_3 x_{n-1} & T_4 x_{n-1} & T_5 x_{n-1} & T_6 x_{n-1} & T_7 x_{n-1} & T_8 x_{n-1} \end{bmatrix}$$

Since there are more observed data points than coefficients, equation (1.2) may not always have a solution. Thus our goal was to find the coefficients A that minimized the difference between the observed data y_i, and the predicted value:

$$z_i = \sum_{j=0}^{k-1} a_j * T_j(x_i) \qquad i=0,1,\ldots,n-1.$$

The LabView Virtual Instrument (VI) that we integrated into our VI uses the least chi-square plane method to obtain the coefficients A. It minimizes the quantity:

$$\chi^2 = \sum_{i=0}^{n-1} \left(\frac{y_i - z_i}{\sigma_i} \right)^2$$

where χ is the standard deviation.

The mean square error (MSE) is obtained using the formula:

$$MSE = \frac{\sum_{i=0}^{n-1} \left(\frac{y_i - z_i}{\sigma_i} \right)^2}{n} = \frac{\chi^2}{n}$$

Once the Chebychev coefficients were obtained, the researcher then used SigmaPlot to obtain a calibration curve for the Cernox 70 ohm resistor. We put the resistance values in column a, the temperature from the 30 ohm resistor in column b, the Chebychev coefficients in column c, and then applied the following user defined transform:

```
L = log(min(col(a)))
U = log(max(col(a)))

for n = 1 to size(col(a)) do
   Z = log(cell(a,n))
   X = (Z-L)-(U-Z)
         (U-L)
for i = 1 to 9 do
cell(d,i) = (cell(c,i))*(cos((i-)*arccos(X)))
end for
cell(e,n) = total(col(d))
end for
```

This transform displays the temperature values according to the curve fit in column e. We reserved column f for delta T, the difference between the observed data and the predicted values. Column g was reserved for delta T/ T, which gave us the percentage of error for each value. We can then determine how well the linear combination of Chebychev polynomials determined in LabView actually fits the data.

Figure 1.2a
Front panel of LabView VI created to determine the Chebychev coefficients A (Desktop/Cheby Polynomial by M. Duffy/curvefitter). When run, this VI prompts the user for an input file, then calculates the coefficients which give the best fit to the input data. These coefficients are then displayed along with a graph which shows the observed data and the fitted curve. The input file should be a text file that contains 2 columns only. The first column should be the resistance values and the second column should contain the temperature values. The Chebychev coefficients obtained for the input resistance and temperature values are as follows:
$a_0 = 171.651$ $a_1 = -104.397$ $a_2 = 16.361$
$a_3 = -2.428$ $a_4 = 0.561$ $a_5 = -0.118$
$a_6 = 0.009$ $a_7 = 0.057$ $a_8 = -0.018$

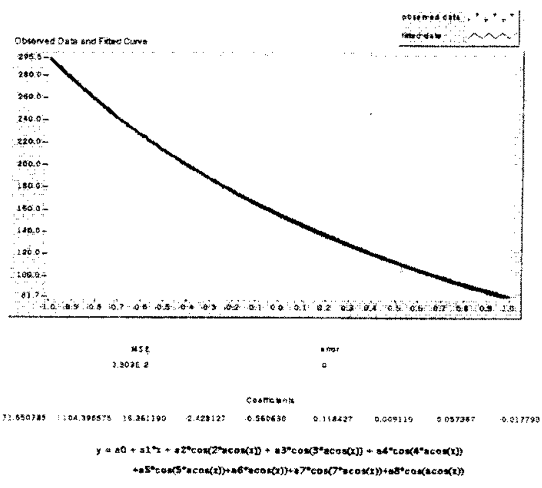


Figure 1.2b. Block diagram of LabView VI created to determine the Chebychev coefficients A. This VI uses several sub-VIs including "Gen LS Linear Fit"; a VI provided in the LabView Library.

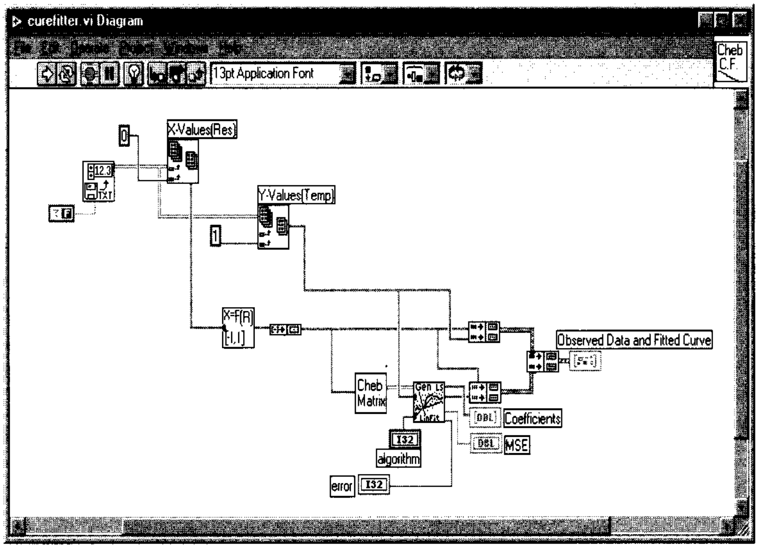
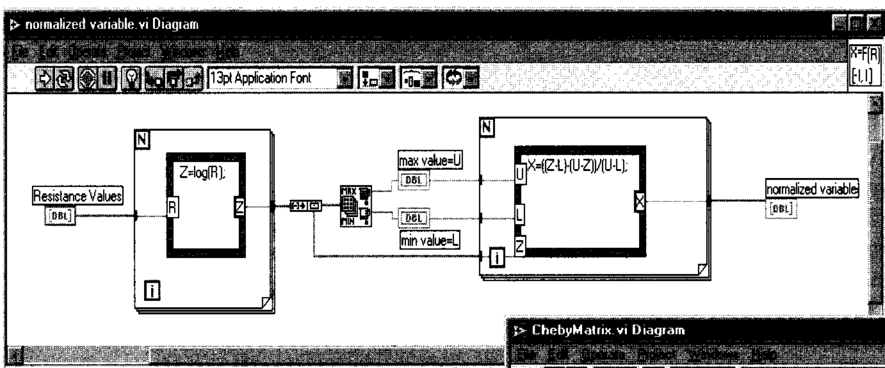


Figure 1.3. User defined VI to normalize the observation data (Desktop/Cheby Polynomial by M. Duffy/normalized variable). This VI normalizes the input resistance values to new values x, such that x is between –1 and 1. A column of observation data (resistance) is input to the VI. The first for loop takes the log base ten of each value and outputs a column of log(R). This column is then simultaneously input into a min/max function and the second for loop. The min/max function picks out the maximum value from the log(R) column and stores it in a variable U; it also picks out the minimum value and stores it as variable L. L and U are then input into the second for loop, which executes the normalizing function



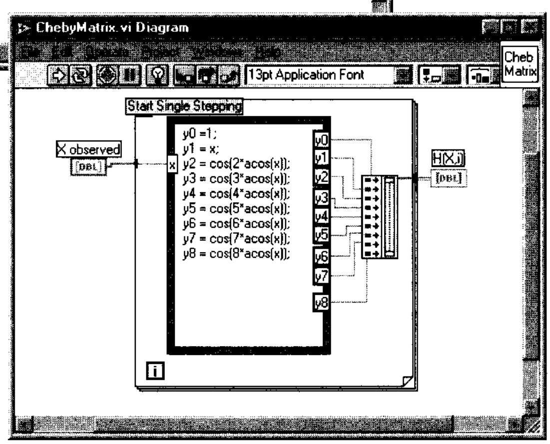
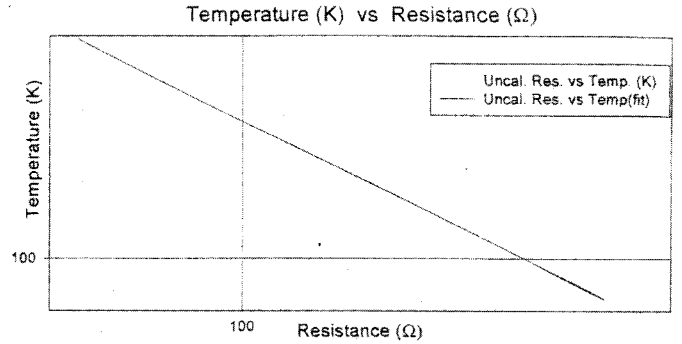
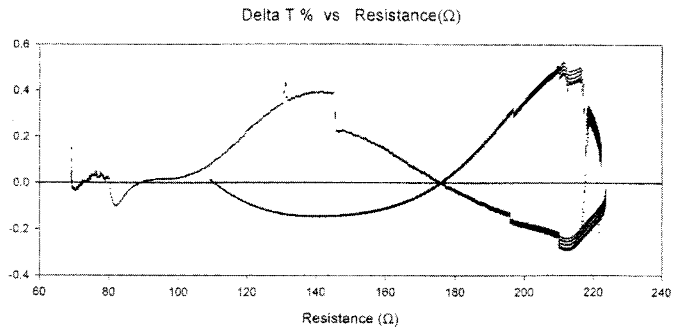


Figure 1.4. User defined VI (Desktop/Cheby Polynomial by M.Duffy/ChebyMatrix) which uses the normalized log(resistance) values to build a matrix H to be used in determining the Chebychev coefficients.

Figure 1.5.
A: SigmaPlot graph of resistance versus temperature observed and also resistance versus temperature predicted. It appears that the predicted temperature accurately estimates the observed temperature.



B: This shows the percent error of our predicted temperature values. It is clear that the error is very small and since it oscillates around zero, we can conclude that our predicted temperature will accurately describe the actual temperature.



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